



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

NOTES ON ISOTOPIC LEAD

BY FRANK WIGGLESWORTH CLARKE

UNITED STATES GEOLOGICAL SURVEY, WASHINGTON

Read before the Academy, April 23, 1918

One of the most remarkable discoveries in the field of radioactivity, has been the fact that the elements of highest atomic weight, uranium and thorium, are unstable, and undergo slow transformations into other substances; especially into helium and lead. The lead thus produced is identical with normal lead in its spectrum and its distinctively chemical properties, but different in its atomic weight; and this difference, which is thoroughly established, is of peculiar significance. The purest lead from uranium minerals has an atomic weight fully a unit lower than that of ordinary lead, while that from thorium minerals is nearly a unit higher. These are the extreme differences, so far as the present evidence goes; but the actual determinations of the atomic weights of these *isotopes* of lead show wide variations due to differences between the minerals from which the lead was obtained. Furthermore, these isotopes differ from ordinary lead in specific gravity; one being lighter and the other heavier than ordinary lead, these differences being proportional to the variations in atomic weight. Consequently the three kinds of lead have the same atomic volume, and occupy the same place in the periodic classification of the chemical elements.

Ordinary or *normal* lead differs from isotopic lead in one important respect, namely, its atomic weight is constant, and the actual determinations vary only within the limits of experimental uncertainty. This constancy was established by Baxter and Grover,¹ who studied lead from a number of distinct sources. Their material was derived from four mineral species; galena, cerussite, vanadinite, and wulfenite, and also from commercial lead nitrate. Furthermore, the minerals examined came from seven widely separated localities; two from Germany, and one each from Australia, Missouri, Idaho, Washington, and Arizona. The lead in each case was carefully purified, and converted into chloride, with which the determinations of atomic weight were made. The method of determination was the standard method long in use at Harvard, and based upon large experience and the most thorough technique. The values found for the atomic weight are shown in the following table:

Source	Atomic weight of lead
Commercial nitrate.....	207.22
Cerussite, New South Wales.....	207.22
Cerussite, Eifel Mountains, Germany.....	207.20
Galena, Joplin, Missouri.....	207.22
Cerussite, Wallace, Idaho.....	207.21
Galena, Nassau, Germany.....	207.21
Vanadinite and wulfenite, Arizona.....	207.21
Galena, Metalline Falls, Washington.....	207.21

A series of analyses of lead bromide gave values practically identical with these.

This evidence as to constancy of atomic weight is conclusive, but it has also been confirmed by three investigations by Richards and his colleagues in this country, and by Hönigschmid in Vienna. These later determinations were made as checks upon determinations of the atomic weight of isotopic lead derived from uranium minerals.

In 1914 Richards and Lembert² published their determinations of the atomic weight of isotopic lead. Their results may be summarized as follows:

Source	Atomic weight
Lead from Ceylonese thorianite.....	206.82
Lead from English pitchblende.....	206.86
Lead from Colorado carnotite.....	206.59
Lead from Bohemian pitchblende.....	206.57
Lead from North Carolina uraninite.....	206.40

Two years later another series of determinations by Richards and Wadsworth³ appeared. The average results obtained were as follows:

Source	Atomic weight
Australian carnotite.....	206.375
Colorado carnotite.....	207.004
Bröggerite, Norway.....	206.122
Cleveite, Norway.....	206.085

Still another series of six determinations by Richards and Hall⁴ on lead from Australian carnotite gave a mean value for the atomic weight of Pb = 206.415.

In a preliminary study of lead from Bohemian pitchblende, Hönigschmid⁵ found values for the atomic weight ranging from 206.719 to 206.749. In a later investigation by Hönigschmid and Horovitz,⁶ lead was extracted from three different minerals, namely, the purest Joachimsthal pitchblende, a crystallized uranium ore from Morogoro, German (?) East Africa, and bröggerite from Norway. The average values for the atomic weight were as follows:

Source	Atomic weight
Pitchblende.....	206.406
The Morogoro ore.....	206.042
Bröggerite.....	206.067

All of these determinations of atomic weight, including those of Baxter and Gover on normal lead, were made by the same method, the same care as to purity of materials, and the same refinements of technique. Even Hönigschmid, now in Vienna, had worked on atomic weight determinations with Richards, and so was familiar with the best procedure. The results obtained are therefore strictly comparable.

For the atomic weight of thorium lead the data as yet are scanty, and based entirely upon material derived from Ceylonese thorite and thorianite.

From the specific gravity of thorite lead Soddy⁷ has deduced the atomic weight of Pb = 207.64; and Hönnigschmid⁸ from analyses of lead chloride prepared from Soddy's original material has found Pb = 207.77. This value, however, is probably too low for the true thorium lead, for the reason that thorite, with a preponderant proportion of thoria, also contains some uranium. The thorite lead, therefore, must contain both isotopes, but with the higher one in much the largest quantity. The thorianite lead studied by Richards and Lembert had a still lower atomic weight, namely Pb = 206.82, which shows that this variety of the metal is not of uniform character.

That the atomic weight of uranium lead is extremely variable has already been shown. In order to interpret this variability its sources must be studied both geologically and mineralogically. On the geologic side of the question the uranium ore can be divided in to three principal classes, which are sharply distinct. The definitely crystallized varieties of uraninite occur in coarse pegmatites, associated with feldspar, quartz, mica, beryl, and other minor accessories. The massive pitchblende is found in metalliferous veins, together with sulphide ores of copper, lead, iron, zinc, and so forth. As for carnotite, that is a secondary mineral, found commonly as an incrustation on sandstone, and often, also upon fossil wood. There may be other modes of occurrence, but these are the most distinctive.

In chemical composition the uraninites, as shown by Hillebrand's⁹ splendid series of twenty-one analyses, fall into well defined groups. All contain uranium oxides, ranging from 65 to 90%, the low figures, however, representing altered material. The crystallized, pegmatitic uraninites are characterized by their content in thoria and other rare earths, from 6 or 7 up to as much as 11%. They also contain subordinate proportions of lead, and the largest amount of helium. In bröggerite and cleveite, however, lead is in excess of thoria. The massive pitchblendes, on the other hand, contain no thoria, usually much lead and little or no helium. That from Black Hawk, Colorado, is exceptional. It is intimately associated with sulphide ores, but contains little lead, and zirconia instead of thoria. Carnotite, which is quite unlike uraninite, is essentially a vanadate of uranium and potassium, with very little lead and no helium. It is, however, an important source of radium.

It is now possible to correlate, at least roughly, the composition of the several minerals with the determinations of the atomic weight of uranium lead, although for a perfect comparison we should have analyses of the actual ores from which the various samples of lead were obtained. On theoretical grounds it is supposed that the true atomic weight of uranium lead is not far from 206, and only determinations which approach that value are those which represent crystallized uraninite, including the varieties bröggerite and cleveite. These minerals all contain helium, so that there seems to be a relation between the formation of these two degradation products of uranium. The

minerals also contain thorium, which would tend to raise the atomic weight and so complicate any discussion of the figures. The most brilliantly crystallized uraninite, that from Branchville, Connecticut, contains 85% of $\text{UO}_3 + \text{UO}_2$, with about 7% of ThO_2 , 4.35% of PbO , and a maximum, 0.4% of helium. The atomic weight of lead from that source, unfortunately, has not been determined; and it is doubtful whether material enough for accurate investigation could be obtained.

The other determinations of the atomic weight of uranium lead give values much above 206, and even approaching 207. This is especially true of the lead from pitchblende, which contains no thorium and little if any helium. Its association with sulphide ores, however, leads to the suspicion that it may contain ordinary lead, perhaps in the form of occluded or dissolved galena. The atomic weight of the lead derived from it would, therefore, be that of a mixture, and not of the isotope alone. The carnotite lead would also seem to be a mixture, but of what kind is not clear.

The atomic weight of isotopic lead now seems to be a complex of at least three quantities, namely, the atomic weights of normal lead, uranium lead, and thorium lead, in varying proportions. Since the atomic weights of the two isotopes differ from that of normal lead in opposite directions it is difficult to determine in any particular case the relative proportions of the three modifications of the element. It has been suggested that normal lead is a balanced mixture of its isotopes; but the constancy of the atomic weight of the ordinary metal seems to negative that supposition. In order to fulfill this condition it would be necessary that the isotopes should always commingle in equal or at least definite proportions; which is extremely improbable. The apparent variations in the atomic weight of lead, as shown in the older determinations, are due to varying methods, imperfect technique, different values for the atomic weights of the other elements with which that of lead is compared, and experimental errors. The modern determinations, which I have already cited, are the only ones that are strictly comparable.

The suggestion that the lead contained in uranium ores is partly normal lead is not new. It has been advanced by other writers,¹⁰ but the variable atomic weight of uranium lead gives the supposition a decided emphasis. It now acquires new importance because of its bearing upon certain attempts to use the ratio between uranium and lead in uranium minerals as a datum for computing the age of the earth. For this purpose the ratio has been employed by Boltwood,¹¹ who calculated it from almost all the trustworthy analyses of uraninite and its nearly allied species, and from it deduced their ages. These ages differ exceedingly. For a crystallized uraninite from Connecticut he found the age to be 410,000,000 years, and for Ceylonese thorianite 2,200,000,000 years. These calculations, and others, like them, involve two assumptions; first, that the rate of change from uranium to lead is accurately known, and secondly that all the lead was of radioactive origin.

The latter assumption is now seen to be extremely doubtful for the varying atomic weights prove that more than one kind of lead must be considered. Thorium lead especially must be taken into account, for many uraninites contain it, and in thorianite the percentage of thoria is more than five times that of uranium oxide. The ratio of lead to its parent elements is therefore much less than Boltwood assumed, and the calculated age of thorianite is vastly reduced. Boltwood, however, doubted the derivation of lead from thorium, a fact which was not definitely known at the time his paper was written. The evidence of the atomic weights is also much later.

Furthermore, the doubtful applicability of Boltwood's method to chronological measurements has been shown by G. F. Becker,¹² who applied it to the analyses of rare-earth minerals from one locality in Llano County, Texas. The figures given by Becker are as follows:

<i>Mineral</i>	<i>Analyst</i>	<i>Calculated age in years</i>
Yttrialite.....	Mackintosh.....	11,470,000,000
Yttrialite.....	Hillebrand.....	5,136,000,000
Mackintoshite.....	Hillebrand.....	3,894,000,000
Nivenite.....	Mackintosh.....	1,671,000,000
Fergusonite.....	Mackintosh.....	10,350,000,000
Fergusonite.....	Mackintosh.....	2,967,000,000

These ages differ enormously, even between two analyses of the same mineral. This evidence, taken together with the evidence from the atomic weights, seems clearly to show that the uranium-lead ratio is not applicable to the determination of the age of minerals. It is quite certain that not all of the lead in uranium ores is of radioactive origin. In pitchblende, for example, which contains no thorium, the determinations of atomic weight range from 206.40 to 206.88, figures far in excess of the theoretical 206.00 which is assigned to pure uranium lead. Normal lead, perhaps in solid solution, must be present in such ores.

What, now, is the fundamental difference between normal lead and isotopic lead? The answer to that question must be largely speculative; but speculation is legitimate when its purpose is to stimulate future research. One difference at least may reasonably be assumed, namely, that normal lead is the product of an orderly evolution of the chemical elements; and that isotopic lead is a product of their decay. Creation is one process, destruction is the other.

Forty-five years ago¹³ I ventured to suggest that an evolution of the elements had actually occurred. It was clearly indicated by the progressive chemical complexity of the heavenly bodies, from the chemically simple gaseous nebulae, through the hotter stars and the sun, to the finished planets like our earth. At first, hydrogen and helium were the most abundant and conspicuous elements, then elements of higher atomic weight gradually appeared, and at the end of the process there was the chemical complexity of the earth, in which the free elements had in great part been absorbed

and replaced by a multitude of compounds. On this basis hydrogen and helium seem to be the oldest of the known elements, while uranium and thorium are the youngest of all. Lead is older than uranium and thorium, for its lines appear in the solar spectrum, in which the other two elements have not as yet been recognized. Lead, however, is vastly more abundant than either uranium or thorium, and is more likely to have been originally their progenitor than their child.

Up to this point we have a reasonable interpretation of definite evidence, beyond this, imagination must come into play. It is fair to assume that the process of evolution was extremely slow, and that each element was developed gradually and passed from an unfinished to a finished stage. The chemical atoms are now known to be extremely complex structures, each with an electropositive nucleus surrounded by electrons in rapid motion. That such a structure could have been developed instantaneously, with no previous preparation, is hardly probable, for the process was one of condensation, from lighter to heavier, and that, it would seem, must have acquired time. The process was one from relative simplicity of structure to relative complexity, and with the maximum condensation, as shown by uranium and thorium, a minimum of stability was reached. That is, so far as we now know; for less stable atoms may have been formed, to exist for a brief period and then vanish. Some of the radioactive elements which appear as products of the decay of uranium are of this kind. On that theme, more later.

That the atoms of the elements above helium in the scale of atomic weights could not have been formed instantaneously is indicated by their structure. It has been shown that they are built up of smaller particles; of electrons, and also in part, perhaps, of preexistent helium. Such particles, approaching one another, at first in irregular proportions, are supposed to have formed the atoms in question; but that exactly the right proportions for stability were found at once is hardly conceivable. There must have been a period of selection, in which the unavailable particles were discarded, probably to be used in other structures later. For each new chemical atom a definite balance between electropositive and electronegative particles was required, and also the establishment of a stable configuration. When these conditions were fulfilled the atom of an element was complete. As I have already said we can fairly assume that there was a distinct passage from an unfinished or incipient structure to a finished one of permanent stability. Furthermore, as shown by the spectra of stars and nebulae, the elements of relatively low atomic weight were first formed, and those of higher atomic weight came later. The older elements were also developed in the largest quantities, and are therefore the most abundant. The later elements are as a broad general rule much scarcer. This rule is not absolutely exact, but it expresses some well known general relations. The very simple and very stable primordial

helium, however, is now relatively rare; but there is evidence to make us believe that it was largely consumed in building other elements. Its present observed emission by radium is evidence in favor of this supposition.

In this evolutionary hypothesis with its subsidiary speculations there is, I think, nothing incompatible with present knowledge. In matters of detail it is unavoidably incomplete; but notwithstanding its imperfections it bears very directly upon a consideration of the later phenomena of radioactive decay. Here the process of evolution is reversed and rapid changes take the place of slow ones. Furthermore, the normal elements are supposed to be veritable store-houses of potential energy; which, in radioactive changes becomes partly kinetic. Radium, for example, gives forth heat continuously; and its rate of decay can be observed in the laboratory.

Through the investigation of radioactive transformations more than thirty new substances, elements or pseudo-elements, have been discovered. Some of these are extremely evanescent, lasting only for seconds or even fractions of a second; others are relatively long lived. All of them, however, are more or less unstable, and change, slowly or swiftly, into other things. Some of them are metallic, like radium, polonium, and actinium; others appear as emanations which belong to the group of the chemically inert gases. One of these, helium, is continuously being generated from radium. Some, again, are isotopic with bismuth or thallium; and four of them are said to be isotopes of lead. These are Radium B, Thorium B, Actinium B, and Radium D. The first three are short lived, and endure only for a few minutes or hours, but Radium D, also known as radio-lead, is assigned a probable life period of 24 years, and given theoretically an atomic weight not far from 210. In its chemical relations it cannot be distinguished from lead.

All four of these isotopes may have been present in uranium lead at the time of its formation, but it does not seem possible that even a trace of them could persist in the lead which is now extracted from uraninite or thorianite. They are therefore negligible in our consideration of the evidence which is now supplied by the study of the atomic weights, except in so far as they show the probable derivation of uranium lead and thorium lead from the two higher elements. The essential point is that all these varieties of lead are products of degradation, and in that respect differ fundamentally from the normal product of evolution. The thirty or more new substances which have been revealed to us by the study of radioactivity are all matter in a state of transition from instability towards some stable form, which may be lead, or bismuth, or thallium, or some other element which has not yet been recognized as an end product of these mysterious changes. As these products are approached we have them in an incomplete condition, nearly but not quite identical with the permanent elements: This may be the character of isotopic lead. The fact that uranium lead is radioactive shows that it is still undergoing change; and that its atoms have not acquired the

exact composition and configuration which give to normal lead its uniformity and stability. Whether or not the process of change can continue until normal lead is formed, it is impossible for us to say.

The atoms of the chemical elements, are, as I have already said, extremely complex, but their structure is not yet completely understood. To some part of each kind of atom its chemical properties and its spectrum are probably due. It is conceivable that this part may be the earliest to form, with its surrounding rings or envelopes at first not quite adjusted to permanent stability. With the final adjustment the isotopes as such should disappear, and the normal element be completed. This is speculation, and its legitimacy remains to be established. A careful comparison of the spectra of the elements from thallium up to uranium might furnish some evidence as to its validity. The spectrum of uranium, for example, may contain lines which really belong to some of its derivatives.

Note.—Since this paper was written, one by Professor Barrell¹⁴ has appeared, in which the use of the uranium-lead ratio for determining the age of minerals is defended. There are also two papers by Holmes and Lawson,¹⁵ and another by Holmes,¹⁶ in which the same position is taken. There is evidently room for further discussion of the subject, but as yet I see no good reason to change my own views.

[Published by permission of the Director of the U. S. Geological Survey.]

¹ *J. Amer. Chem. Soc., Easton, Pa.*, **37**, 1915, (1027).

² *Ibid.*, **36**, 1914, (1329).

³ *Ibid.*, **38**, 1916, (2613).

⁴ *Ibid.*, **39**, 1917, (531).

⁵ *Zsch. Elektrochem., Halle*, **20**, 1914, (457).

⁶ *Monatsh. Chem., Vienna*, **36**, 1915, (355).

⁷ *Nature, London*, **94**, 1915, (615).

⁸ *Chem. Abst.*, **11**, 1917, (3173). From *Physik. Zs.*, **18**, 1917, (114).

⁹ *Washington, U. S. Geol. Survey, Bull.* 78 and 90. Also in *Bull.* 591, pp. 366-368. Hillebrand discusses the mode of occurrence of these minerals, much as I have done.

¹⁰ See Joly, *Phil. Mag.*, (6), **22**, 1911, (354). and Becker, *Bull. Geol. Soc. Amer.*, **19**, 1908, (134).

¹¹ *Amer. J. Sci., New Haven*, (4), **23**, 1907, (86).

¹² *Bull. Geol. Soc. Amer.*, (4), **19**, 1908, (134). See also Zambonini, *Rome, Atti Acc. Lincei* (5), **20**, part 2, 1911, (131).

¹³ *Popular Science Monthly*, January, 1873.

¹⁴ *Bull. Geol. Soc. Amer.*, **28**, 1918, (745).

¹⁵ *Phil. Mag.*, (6), **28**, 1914, (823), **29**, 1915, (682).

¹⁶ *Proc. Geologist's Assoc., London*, **26**, 1915, (289).